Electronic Supplementary Information (ESI) for

Thiol-Ene Click Reaction: A New Pathway to Hydrophilic Metal-Organic Frameworks for Water Purification

Mingyuan Fang,[a] *Riansares Muñoz-Olivas,*[b] *Carmen Montoro,* [c,d]* *and Mona Semsarilar* [a,]*

[a] Institut Européen des Membranes—IEM UMR 5635, Univ Montpellier, CNRS, ENSCM, 34095 Montpellier, France

[b] Departamento de Química Analítica, Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid, Spain

[c] Departamento de Química Inorgánica, Universidad Autónoma de Madrid, 28049, Madrid, Spain.

[d] Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain.

*Correspondence: carmen.montoro@uam.es (C.M.); mona.semsarilar@umontpellier.fr (M.S.)

Table S1. Summary of Zr-MSA PSM by click reactions.

Sample	PEG	Catalyst or initiator	Physical aspect after click
Zr-MSA-UV1	PEG-acrylate-480	DMPAP/UV	Suspension
Zr-MSA-UV2	PEG-diacrylate-575	DMPAP/UV	Gel
Zr-MSA-P1	PEG-acrylate-480	TBP	Suspension
Zr-MSA-P2	PEG-diacrylate-575	TBP	Suspension

Table S2. Textural parameters for the Zr-MSA and the Zr-MSA modified by click reactions.

Sample	$S_{BET,}$ m^2 g^{-1}	Micropore volume, cm^3 g^{-1}	Total pore volume, cm^3 g^{-1}
Zr-MSA	547	0.146	0.37
Zr-MSA-UV1	97	0.018	0.18
Zr-MSA-UV2	90	0.015	0.12
Zr-MSA-P1	232	0.05	0.22
Zr-MSA-P2	269	0.06	0.27

Digestion of PEG clicked Zr-MSA

10 mg of each sample were added into an eppendorf with 0.4 mL of DMSO-d_6. Then, 50 µL of HF and 0.1 mL of D_2O were added to the mixture. The mixture was sonicated for 2 minutes and kept at room temperature for 2 hours. The supernatant was analyzed by ^1H NMR.

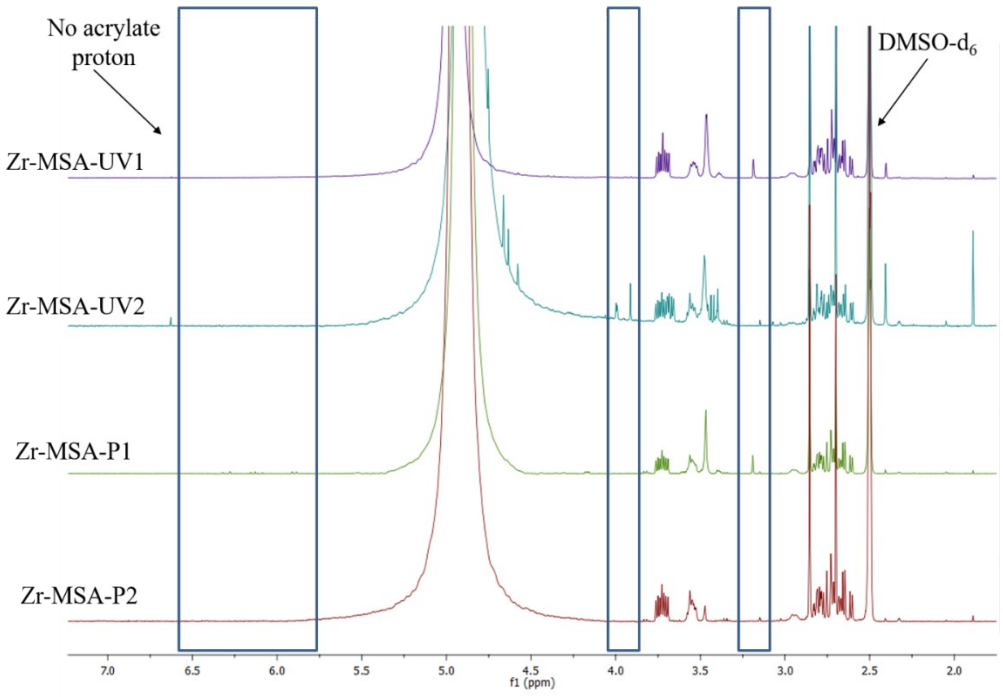

Figure S1. ^1H NMR spectrum of Zr-MSA-UV1, Zr-MSA-UV2, Zr-MSA-P1 and Zr-MSA-P2 (from top to the bottom) after digestion in HF.

No acrylate signals could be found at the region between 6 and 6.5 ppm. Indicating that all the PEG was attached to the thiols of the MOF structure. A singlet signal around 3.2 ppm could be seen in Zr-MSA-UV1 and Zr-MSA-P1 indicating the proton s of the methyl (C**H$_3$**) in the PEG-acrylate-480. For Zr-MSA-UV2, signals around 4 ppm were attributed to C**H$_2$**-C**H$_2$** that appeared after the click reaction. Note that these signals were between the multi signals of MOF linker, the PEG C**H$_2$** signals (from 3.4 to 3.8 ppm) and the board intense signal of HF (4.8 to 5.6). This leads to an underestimation of the number of clicked PEG-diacrylate-575, explaining difference between the figures estimated from TGA and NMR data. The wt. % amount of PEG was calculated using the theoretical Zr-MSA formula; $Zr_6O_4(OH)_4(MSA)_6$.

H NMR shifts of MSA and PEG back bone;

MSA: HOOCCH(SH)C**H$_2$**COOH, 2.6- 2.8 ppm; HOOCC**H**(SH)CH$_2$COOH, 3.57 ppm; HOOCCH(S**H**)CH$_2$COOH, 3.29 ppm

PEG: ---(C**H$_2$**C**H$_2$**O)$_n$CH$_2$CH$_2$---, 3.4- 3.8 pm; ---(CH$_2$CH$_2$O)$_n$C**H$_2$**CH$_2$---, 3.6 ppm; ---(CH$_2$CH$_2$O)$_n$CH$_2$C**H$_2$**---, 4.2 ppm

Table S3. Amount of clicked PEG (wt. %) calculated using TGA and ^{1}H NMR after digestion in HF.

Sample	**PEG**	**PEG (wt. %) TGA**	**PEG (wt. %) ^{1}H NMR**
Zr-MSA-UV1	PEG-acrylate-480	2	3.8
Zr-MSA-UV2	PEG-diacrylate-575	23	7.3
Zr-MSA-P1	PEG-acrylate-480	0.5	2.9
Zr-MSA-P2	PEG-diacrylate-575	0.5	NA

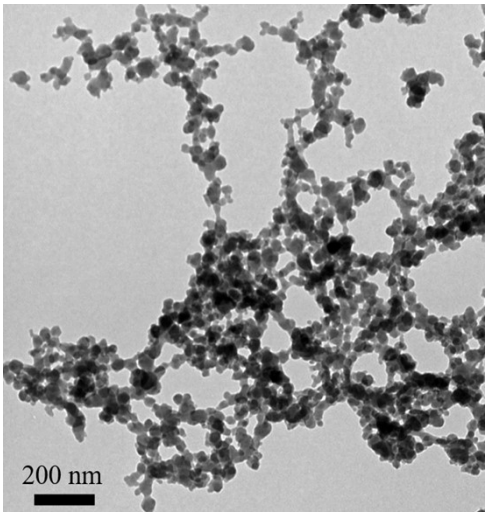

Figure S2. TEM image of Zr-MSA.

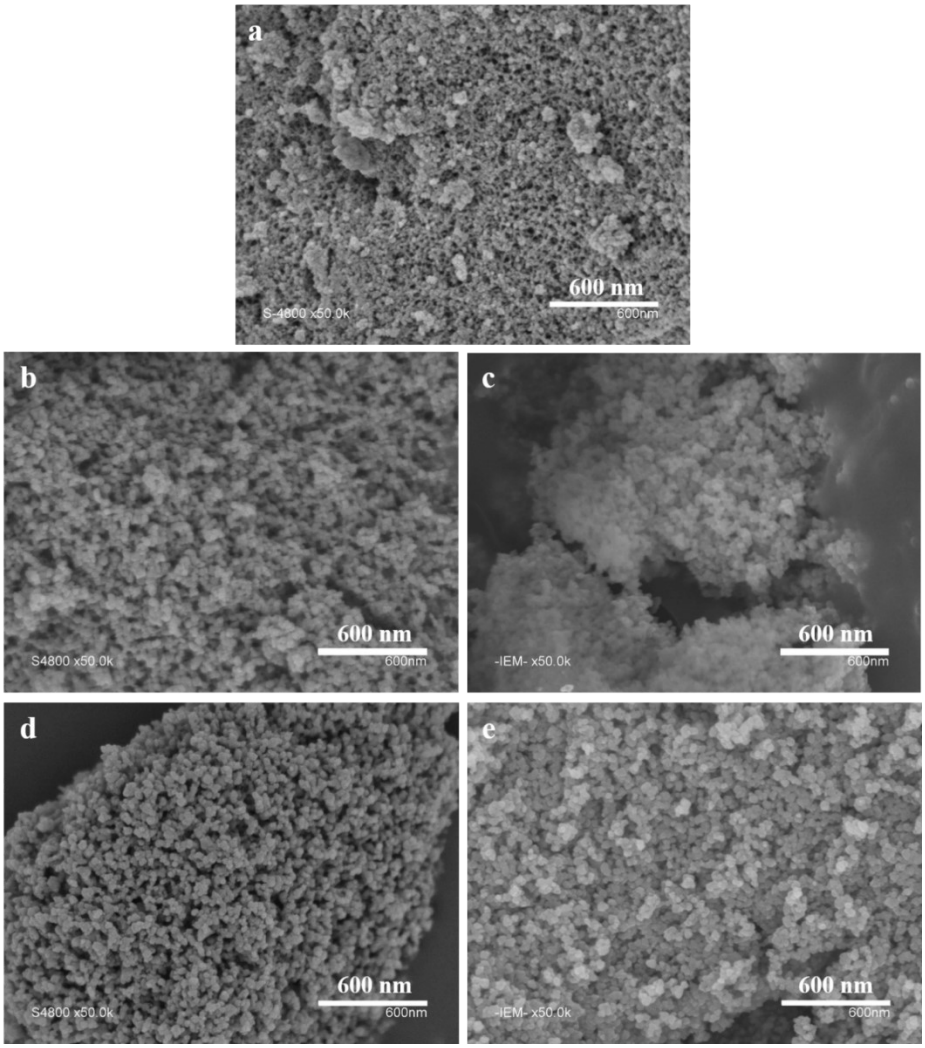

Figure S3. SEM (a) Zr-MSA, (b) Zr-MSA-UV1, (c) Zr-MSA-UV2, (d) Zr-MSA-P1 and (e) Zr-MSA-P2

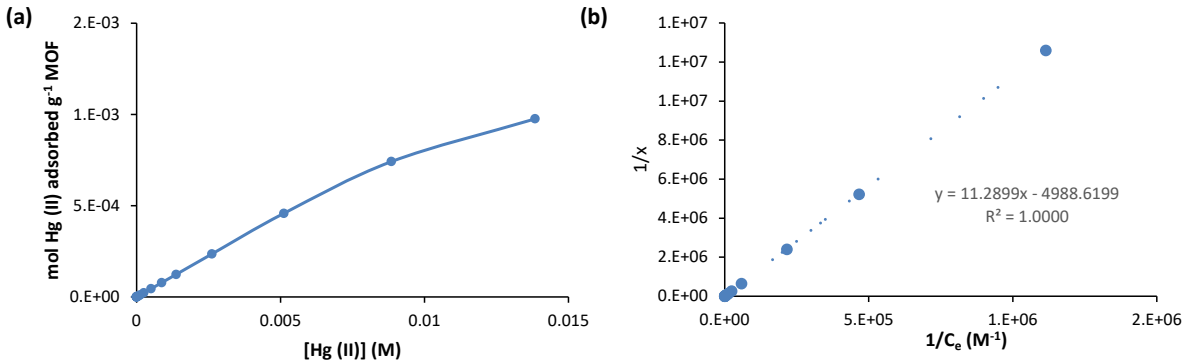

Figure S4. (a) Hg (II) adsorption isotherm for Zr-MSA-UV2 and (b)linear regression by fitting the equilibrium adsorption data with the Langmuir adsorption model.

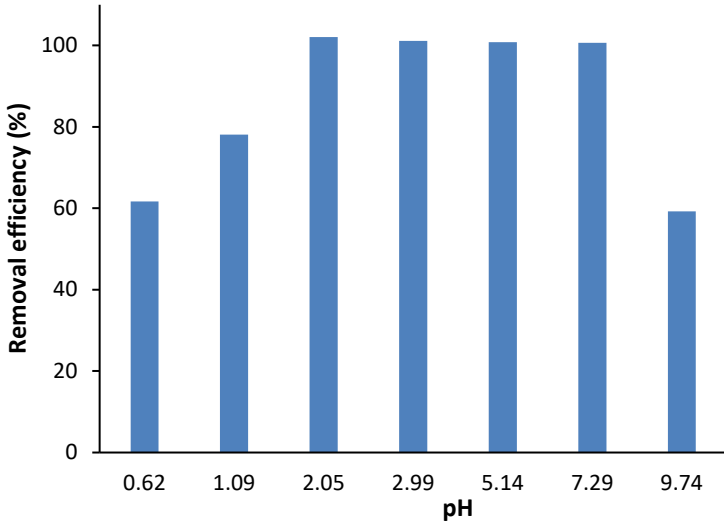

Figure S5. Removal efficiency of Hg (II) by Zr-MSA-UV2 under different pH conditions.

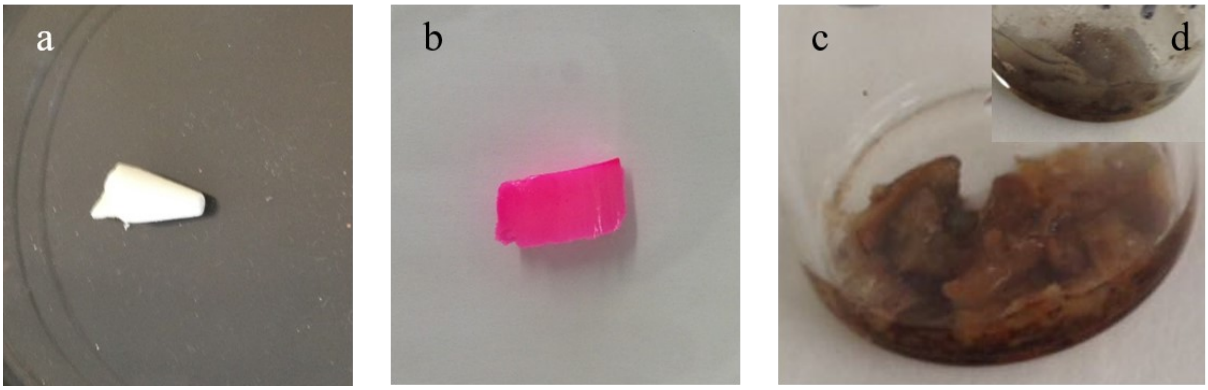

Figure S6. (a) Zr-MSA-UV2 gel, (b) Zr-MSA-UV2 gel after RhB adsorption, (c) Zr-MSA-UV2 gel after Cr absorption, (d) Cr absorbed Zr-MSA-UV2 gel after 2 days.